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The Inductive Effect in Organic Chemistry

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Comments upon Models:

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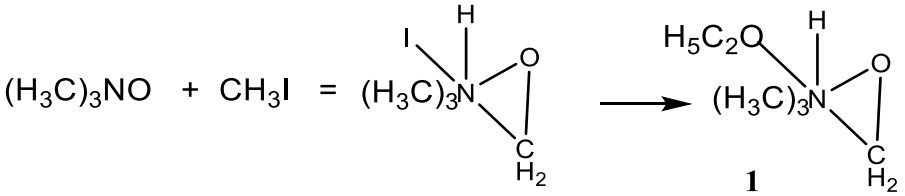
Abstract: The subtle difference between the successive polarization model and the flow of electrons through sigma bonds is explored, as well as the alternating charge model of Pople and the pervasive field model. The present paper is concerned with the ability of alkyl groups to serve as sigma inductive electron donors.

The "inductive effect" remains an icon of chemical education and chemical thought. It is appreciated by students as a concept easily grasped, and it is a concept that is well liked by instructors as easy and rapid to present. However, the history of the "inductive effect," in its various incarnations is hardly as smooth as these complacent attitudes might suggest. It is an example of how an attractive and firmly held idea is transmitted from generation to generation, despite legions of commentaries in the literature, most favoring another interpretation, "the field effect". The classical concept of the inductive effect persists, nonetheless.[1,2] An example of the diminishing effect of alkyl groups: the addition of a methyl group to nitromethane, enhances the dipole moment (slightly) from 3.46D(g) to 3.60D(g).[3-6] Extending the chain to nitropropane has no effect (3.60D(g)..

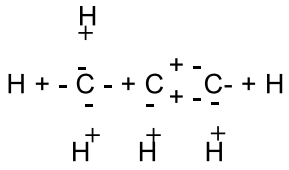
The struggles of earlier chemists to understand the distribution of charge in molecules is a fascinating story. One apocryphal account concerns Arthur Michael, near the early 1900's. Michael stated that a substituent is capable of "infecting" other parts of the molecule.[7,8] The germ theory of disease had, by then, become well known in scientific circles. Michael was one of the first American chemists who attempted theoretical explanations of molecular behavior.[9,10] These explanations often involved thermodynamic principles, especially entropy. Michael was a trenchant critic of European ideas, particularly purely mechanical ideas of the course of chemical reactions. Later in his long career, Michael may have come to regret his comments about tetrahedral carbon as well as Baeyer's strain theory.[11,14]



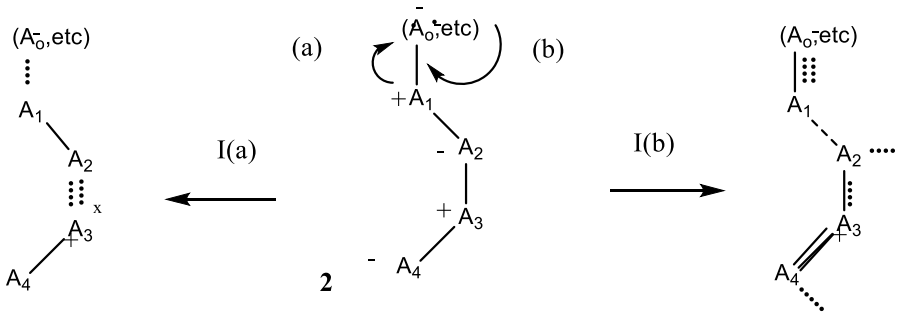
Arthur Michael (1920)

The origin of the "inductive effect" is often attributed to G.N. Lewis, who used the concept to explain the effect of substituents upon acidity of carboxylic acids.[15] The early scientists (like today), used the concept of charge density to explain the course of chemical reactions, e.g. the addition of HCl to propene to give 2-chloropropane, not 1-chloropropane, the so-called "positive-negative" theory [10,16-20] The H^+ from HCl was presumed to be attracted to the more negative (terminal) alkene carbon atom of $RCH=CH_2$ (cf. Cuy's structure of Scheme I).[16] More or less simultaneously, the Cl^- was attracted to the more positive (central) atom. The relative stability of carbocations was a concept 10-15 years in the future.

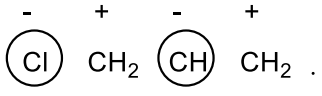
Scheme 1: Assumed Charge Densities, ca. 1920



Eustace Cuy (1920)

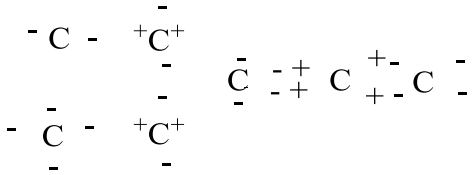


Arthur. Lapworth, (1922)



William Kermack and Robert Robinson (1922)
(polarization of allyl chloride)

Scheme 1: (continued)



Lucas and Jameson, (1924)
diethyl allene

Diagrams such as **2** (Scheme 1) assaulted the senses of students of the 1920's. Contributors included Harry Shipley Fry, Hanke and Koessler, Steiglitz, Conant, Lapworth, Lucas, as well as.Cuy.[16-25] Concepts such as "residual affinity" or "partial valencies" were concepts of this early period.[17-21] Perhaps the clearest view of "induced polarity" by substituents, stemmed from the work of Kermack and Robinson (Scheme 1) as well as Lucas and Jameson[24,25]

The origin of the inductive effect is attributed to Lewis or sometimes to Branch and Calvin.[26] The concept emerged into its present form through the work of Hughes and Ingold, who (following Remick) suggested the terminology I_s (where "*I*" signifies inductive, and "s" means static, or always present).[27,28] The $-I_s$ effect indicated electron withdrawal by the substituent, whereas $+I_s$ indicated electron donation. Among Ingold's other "substituent effects" are the "mesomeric" (resonance) effect (*M*), which remains prominent today. The "inductomeric" and "electromeric" effects (called forth in the course of chemical reactions, as opposed to "static" effects) have fallen into disuse. The "*field effect*" (operating through space) originated at an early date, perhaps in response to the development of electrical theories in physics.[6,13] The origin of the field effect is difficult to pinpoint.[9] More recently, the *field effect* was associated with M.J.S. Dewar (among many other contributions).[29-33]. Dewar established the ***F*** scale of substituent effects to replace σ_I *(inductive* parameters).[29] Dewar later modified his basic ideas to include secondary field effects in his MFFM model.[29,30] Godfrey went beyond the usual dissection involving polar *(field, inductive*) and resonance effects into Coulombic, overlap field and charge transfer effects.[34] This concept never gained widespread acceptance.

In the Ingold conception of the $-I_s$ effect the sigma bonds are polarized in a progressively increasing manner toward the electronegative group X. Ingold made it clear that there should be **no** flow of electrons from one sigma bond to the next, but rather a progression of increasing polarization of sigma bonds.[27]

$$CH_3 > CH_2 > CH_2 > CH_2 > X \qquad (1)$$

Another concept suggests that electron density **is** passed down the carbon chain one atom to the next as in model (2). In other words, the carbon chain acts as a conductor or semiconductor. This model is widespread, particularly in undergraduate courses (and graduate student seminars) but its precise origin is unclear .This model may be based on the application of molecular orbital theory, which considers electrons as occupying orbitals that encompass sets of atoms or the entire molecule.[2,6,15,35-39] In 1940, Hammett (as well as Lewis) provided a verbal description of the inductive effect that could be considered as consistent with model (2)[15,32,40] Smith and Eyring, however, retained the polarization model (1) in one of the first applicatons of MO theory to chemical structure and provided a general theory of the inductive effect following LCAO procedures.[35-39] Wiberg has dissected the calculated charge densities on carbon atoms into sigma and pi components, not unlike aromatic systems, although the MO based procedure is complex.[41]

$$\delta\delta\delta+ \quad \delta\delta+ \quad \delta\delta+ \quad \delta+ \quad \delta-$$

$$CH_3 - CH_2 - CH_2 - CH_2 - X \qquad (2)$$

Today, published documents retain Lewis' representation of chemical bonding by means of "lines" as there is no good way to portray molecular orbitals.in typesetting for texts or in lectures. This practice inhibits adjustment of thinking toward a MO model, whereby orbitals encompass many atoms.

Perhaps many chemists view the difference between models (1) and (2) as inconsequential, although the difference is quite real. Today, most undergraduate texts are circumspect and say little.[42-44] Remick, in his influential 1943 book on electronic interpretations of organic chemistry, favored (1), as did more modern texts: e.g. Jack Hine in 1962 and Jerry March in 1985.[28,45,46] Carey and Sundberg consider the inductive effect to be electrostatic in nature.[47,48]

Hansch, Leo and Taft were highly successful in correlating ^{19}F nmr chemical shifts in substituted benzenes yielding both "field/inductive", and resonance, parameters of substituents.[49] This work led to formulation of over 500 resonance and "inductive" parameters, the latter achieved through study of meta substituted fluorobenzenes, where any resonance effect between ^{19}F and the meta ring position should be minor. This was perhaps the most successful of many attempts to correlate inductive effects with Hammett parameters.

One of the most authoritative commentators has been W.F. Reynolds in his 1983 publication in *Progress in Physical Organic Chemistry*.[50] Correlations with Hammett parameters were prominent in this

publication. However, Reynolds considered the effect of meta benzene substituents on nmr chemical shift to be field effects, not movement of electrons through sigma bonds. Reynolds noted that two common methods of assessing charge densities, i.e. acidities of substituted carboxylic acids and also nmr chemical shifts, independently suffer from difficulties limit their usefulness..

Following G.N. Lewis' original ideas, many undergraduate texts continue to cite the effect of electronegative substituents (e.g. in chlorobutanoic acids) on carboxylic acid acidity as a simple *inductive effect*, although more commonly in recent years, texts introduce the topic, but say little.[42,44] The concept remains attractive to many teachers.[51] However, as has been long known for quite some time, entropy effects upon acidity are significant and even dominant. As J. March pointed out in his book "Advanced Organic Chemistry, Reactions, Mechanisms and Structure" (1977):[46] "As an example, the data in Table 5" (p. 25) "show that more than half of the acid-strengthening effect of the Cl in $ClCH_2COOH$ comes from entropy and less than half is caused by ΔH. A more extreme example is trichloroacetic acid, which is about 10,000 times stronger than acetic acid, but which actually would be a weaker acid if enthalpy effects were all that mattered." It is difficult to formulate a fundamental property such as the inductive effect on presumed effects on entropy. Despite this clear warning in 1977 (and earlier) undergraduate texts routinely cited the acidity data in α, β, γ-chlorobutanoic acids as evidence for the *inductive effect*.[51]

Our own calculations (MM3 and MMX, plus quantum calculations) are quite variable, depending upon calculation program used and especially on dielectric constant of the medium. At DK 20 (essentially ethanol as solvent), the extended zig-zag carbon-chain form is most stable, but the twisted or gauche form is calculated to make a substantial contribution, placing the positive carbon of the C3 C-Cl dipole near carboxylate.[39] This conformation is dominant at DK 1.5.[52,53] The data are consistent with the importance of **ion-dipole attraction** in the anions as important stabilizing factors.[3] This could be considered as a type of *field effect*.

Bordwell and co-workers have explored the effects of alkyl groups on the acidity of carbon acids in great detail.[53-56]. The case of the effect of alpha methyl substitution in nitromethane and in certain ketones is most provocative. Methyl substitution enhances acidity, which would be odd behavior for an electron donating group. Stabilization of $RCH{=}NO_2^-$, i.e. the enolate, is considered of importance. In simple alcohols in the gas phase, Brauman noted enhanced acidity as alkyl groups were added, the opposite of solution data.[57,58] Polarizability effects in the gas phase were considered dominant.

In one of the early applications of molecular orbital theory to chemical phenomena, Pople and Gordon (1967) postulated alternating charge effects due to the electronegativity of X, (cf. model 3).[59] Inexplicably, Reynolds failed to mention this model in his 1983 review, although other aspects of Pople's work were included[50]. In fact, despite the eminence of both Pople and Gordon as theoreticians, almost no publication today makes mention of model (3). An exception is Anslyn and Dougherty, "*Modern Physical Organic Chemistry,*" (2006).[60-61]

δδδδ– δδδ+ δδ– δ+ δ–

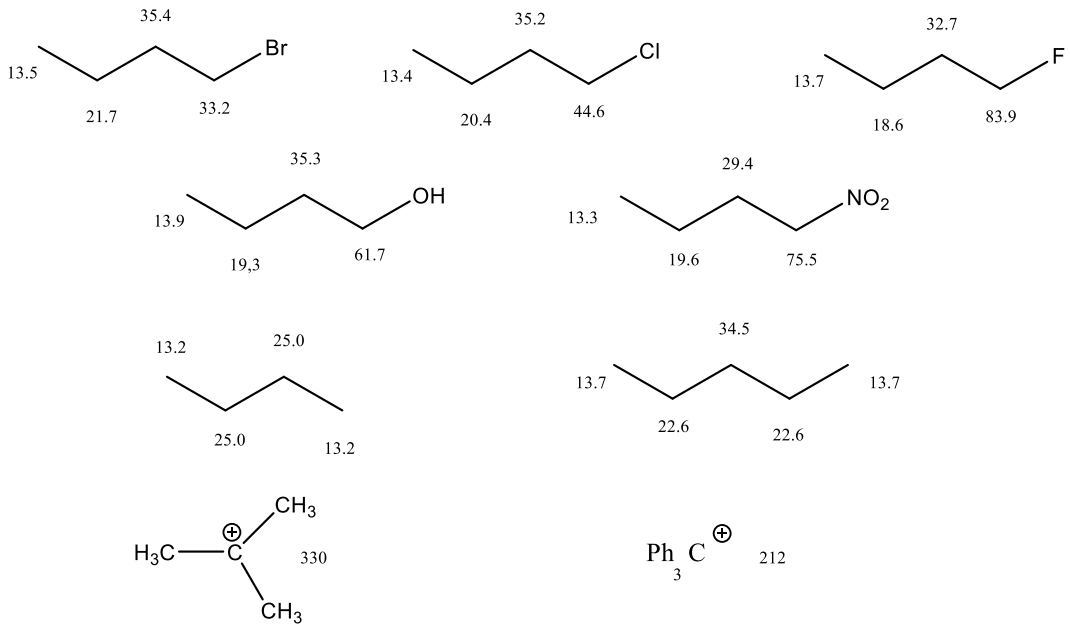
$$CH_3 - CH_2 - CH_2 - CH_2 - X \qquad (3)$$

Pople and Gordon's CNDO level calculations, were quite advanced for 1967, but would be regarded as low level today. Also, quantum calculations provide accurate dipole moments but do not explicitly calculate charges on individual atoms. Nonetheless, calculations of charge densities using the venerable Mulliken methodology (also NPA, and also the MK model) at the RHF/6-31G level do indicate that the beta carbon is more negative than the alpha and gamma carbons[63]. MP2 calculations agree in general trends.

Some slight support of the alternating charge model (3) can be found from ^{13}C nmr chemical shifts. Introduction of positive charge density in an organic molecule usually is associated with a downfield chemical shift for a given carbon, e.g. the carbocations shown in Scheme 2.[64] It should be noted that one prominent worker in the field, George A. Olah, did not believe that ^{13}C chemical shifts were a good index of positive charge density.[65-67]

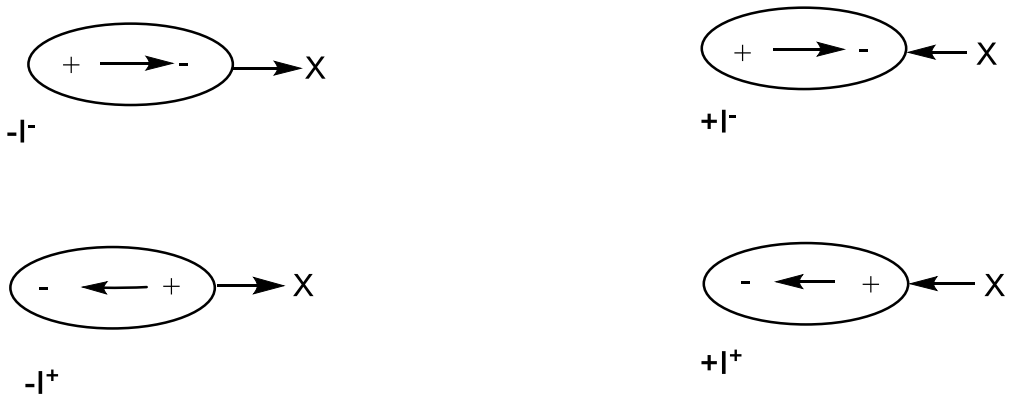
Introduction of an electronegative group at the terminal carbon of alkanes indeed shifts the alpha carbon strongly downfield in alkyl chlorides, alcohols and nitro compounds. However it is the gamma carbon that moves upfield, perhaps indicative of enhanced charge density at that carbon. The magnitude of the upfield shift is proportional to the electron withdrawing ability of the substituent X. There is some confusion on which standard to judge the substituted hydrocarbon against, i.e. is butane or pentane the best standard? The conformations of these materials is not precisely as shown in Scheme 2. The electronegative substituents like to be anti to a hydrogen (presumably for hyperconjugation). The energy difference between the trans zig-zag conformation (shown in Scheme 2) and the gauche conformation (not shown) is -0.28 kcal (X=Br), -0.26 (X=Cl), -0.09 (X=F), -0.30 (X=OH) and -0.16 ($X=NO_2$) (from MMX force-field calculations at DK = 1.5). The zig-zag conformation was dominant in each case However, mp2/6-31++G(d,p) calculations favor the gauche conformation for X = F, (+0.4 kcal more stable). The ^{13}C chemical shift changes (relative to C2 of pentane) are -0.9, -2.2, -4.0, -3.3, and -3.0 (same order of X substituents).: The gauche conformation places the X group increasingly close to the gamma carbon. The beta carbons show a somewhat similar upfield shift, though smaller in magnitude. The nmr data were collected from several sources, and perhaps the conditions of the spectral determination were different. ^{13}C chemical shifts are complex, and it is difficult to interpret them in terms of a single effect such as charge density.[50,68]

Scheme 2: ^{13}C NMR Chemical Shifts



Pople and Gordon went on to propose four different types of inductive substituent behavior, as shown in Scheme 3. It is clear that charges induced on the alpha carbon by substituents such as fluorine and trimethyl ammonium are quite different

Scheme 3: Pople and Gordon's induced Charges



In the same issue of JACS as Pople and Gordon's work, Newton and Lipscomb, published a theoretical study on methylacetylene relating to the common concept of methyl as an electron donor to the pi system.[68] Multiple factors were considered: molecular orbital coefficients, eigenvalues, total

energies, dipole moments as well as population analysis. Their approach suggests that **sigma electron donation by methyl is not significant**.[69,70] One statement of interest is that the dipole moment of methyl acetylene results from rearrangement of existing acetylene pi electron density, not from sigma charge donation by methyl. Unfortunately, undergraduate texts routinely represent methyl simply as a simple sigma electron donor.[69-71]

In a computational studies of electrophilic aromatic substitution by Hehre, Radom, and Pople and by Streitwieser and coworkers, reasons for the ca. seventeen-fold greater reactivity of toluene over benzene and ortho/para directive effects of the methyl group of toluene were explored.[72-75] Hehre, Radom and Pople emphasized polarization of the pi system by the methyl of toluene. The calculated pi electron density is about equal for the ortho and para position of toluenes, but most reactions give more para product (nitration is the exception).[62,,75] The high and negative ρ^+ values found for most aromatic substitution argues against the importance of coefficients.[72-75] Taft and Topsom believe that Hammett parameters may not be constant in the course of a chemical reaction, and even may change in sign.[76,77]

The popular conception of the methyl group as a sigma electron donor remains widespread.[47,62] The greater stability of tertiary carbocations than secondary than primary is attributed to the electron donating effects of methyl (inductive plus hyperconjugation),(with exceptions).[62] Another possibility would be the destabilizing effect of hydrogen as it withdraws electrons in primary carbocations. The group electronegativities of H vs. CH_3 are very similar (2.3 vs. 2.28).[28,78] In the Mulliken scale (atoms, not groups) H should be a stronger electron withdrawer, H (3.01) vs C (2.67).[60,78] Sunko attributes the greater reactivity of methyl substituted substrates in solvolytic reactions to hyperconjugation by CH_3.[79] However, in studies of the effect of alpha deuterium substitution on amine basicity, Perrin and coworkers disfavored C-H vs. C-D inductive effects as factors affecting amine basicity.[79-81] The stereochemical effect upon basicity of C-H vs. C-D substitution was shown to be of importance. However, the question remains as to whether the inductive effect should be uniform (although attenuated) throughout a carbon chain, or if stereochemical relationships do play a role, particularly approaching the transition state.[55-58,82] Micro changes in internal dielectric constant may be of importance, depending on H orientation.[82,83]

Calculation of charge densities is shown in Scheme 4, for what they are worth. The Mulliken method of approximating charge densities shows **increasing** positive charge density on the **carbocation carbon** in the order methyl < 1^0 < 2^o < 3^o despite hyperconjugation, an undeniably real effect.[55,82] In Scheme 4, the entries for CH_3 represent the sum of carbon plus hydrogens charges. The NPA and CHELPG methods show more complex results, although past methyl, the order of increasing positive charge density on the carbocation carbon is also 1^0 < 2^o < 3^o. Bader's "atoms-in-molecules" (AIM, charges option) approach appeared to distribute the positive charge more or less equally over all atoms in the molecule.[84-86]

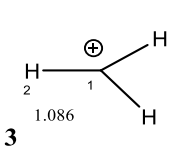
This “wrong way” expression of positive charge density (against experimental evidence for carbocation stability) has been recognized for quite some time.[65,66,] Much depends, of course, on how the calculation program interprets the charge density for carbon vs. hydrogen in a given C-H bond. If the positive charge at the central carbon is summed with that of attached hydrogens, then the positive charge densities for the central carbon (plus attached hydrogens) is +1.0 for $+CH_3$, +0.706 for $+CH_2CH_3$, +0.496 for $+CH(CH_3)_2$ and +0.326 for $+C(CH_3)_3$ (Mulliken method). This is consistent with the order of ease of formation of carbocations and saves the appearance of methyl(s) as inductive electron donors.

The NBO (natural bond orbital) approach of Glendening, Reed, Carpenter and Weinhold (available in the Gaussian programs) represents a type of “reverse engineering” whereby the “many-electron wavefunction” is analyzed in terms of “localized electron pair “bonding” units.[87-89] The result of this dissection is “natural atomic orbitals” and “natural hybrid orbitals”, familiar to most organic chemists since Pauling’s’ era.[90] The NBO data in Scheme 4 (bottom) represent the C^+-H and C^+-C bonds. Thus, for **3** ($CH_3^{+)}$, a C^+-H covalent bond results from a 63% contribution from carbon and a 37% contribution from hydrogen. These “contributions” are derived from MO coefficients.

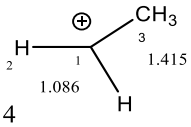
It is noteworthy that the C+-C bond distance lengthens progressing from primary to tertiary, although the C+-H bond changes little. The “contribution” of C+ to form the C+-CH_3 bond increases slightly. The “hybridization” of C+ (in the C+-CH_3 bond) changes from $sp^{1.69}$ to $sp^{1.83}$ to $sp^{1.99}$, consistent with the increases in bond distance. This increase places bonding electron density progressively further from C+, thus increasing apparent positive charge density on C+. It is not obvious what originates and

what is derived:: bond distance, “hybridization”, or “contribution”.

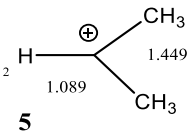
Scheme 4: Calculated Charge Densities by Three Prominent Methods



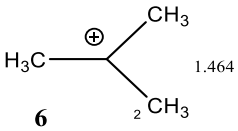
3



4



5

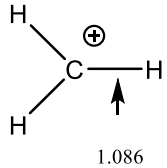


6

	3	4	5	6
Mulliken	C +0.227 H +0.257	C +0.248 H +0.229 CH_3 +0.296	C +0.287 H +0.209 CH_3 +0.252	C +0.326 CH_3 +0.225
NPA	C +0.307 H +0.231	C +0.297 H +0.250 CH_3 +0.206	C +0.436 H +0.259 CH_3 +0.152	C +0.674 CH_3 +0.108
CHELPG	C +0.644 H +0.119	C +0.516 H +0.119 CH_3 +0.270	C +0.618 H + 0.088 CH_3 +0.148	C +0.624 CH_3 +0.145
	C1—H2 61% sp^2 39% s	C1 — H2 62% $sp^{2.20}$ 38% s C1 — C3 49 % $sp^{1.69}$ 51% $sp^{2.66}$	C1 — H2 63% $sp^{2.30}$ 37% s C1 — C3 50% $sp^{1.83}$ 50% $sp^{2.70}$	C1 — C2 51% $sp^{1.99}$ 49% $sp^{2.60}$

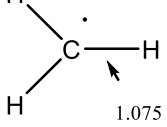
The data of Scheme 5 lists the C-H bond distances in free radicals, cations and anions derived from methane. It is noteworthy that C-H bond distances are short in free radicals, but otherwise approximately the same. The bonding situation in free radicals is not at all understood, at least by this writer. Scheme 5 also shows the “contributions” of carbon vs. hydrogen in making up the C-H bond. The “hybridization” of carbon is roughly constant**.** All are calculated to be planar (even **10**), except, of course, **9**.

Scheme 5: Bond Distances and "Contributions" to Bonds in Simple Ions and Molecules



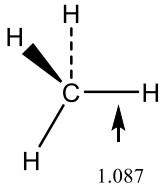
7

C 63% sp^2 H 37% s



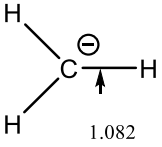
8

C 56% sp^2 H 44% s



9

C 60% sp^3 H 40% s



10

C 58% sp^2 H 42% s

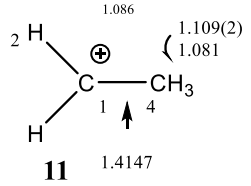
Scheme 6 shows the ethyl series of structures, including fluorinated molecules. Scheme 6 shows that C-C distances are much shorter in the cation **11** and the fluorinated anion **14** than in other species. due to hyperconjugation and inverse hyperconjugation, respectively.[83,91] On the other hand, **14** and **15** show somewhat extended bond distances due to inhibition of the above effects.

In **11**, C+ utilizes a "short" $sp^{1.69}$ orbital to form the C+-CH_3 bond. In **15**, a "longer" $sp^{2.16}$ orbital is assigned by the NBO program. In **14**, CH_3 is calculated to use a much shorter $sp^{1.96}$ orbital than CH_3 of **11** ($sp^{2.66}$). This could be attributed to electron donation by CH_3 of **11**.

Compound **18** is the opposite number of **11** in many ways. *I*n **18**, CF_3 uses a short orbital to form the C-C bond, thus placing charge density away from C^- and closer to CF_3. Unfortunately, hyperconjugation in **11** and inverse hyperconjugation in **18** clouds the inductive donation by CH_3 or withdrawal by CF_3 picture.[83,91] In **18**, the C-F bond distances are long (1.457A(2) and 1.387A) especially compared to **17** (1.361A(3) and especially to **15** (1.336A(2) 1.321A) in which inverse hyperconjugation is of lesser importance.. For **11**, the C^+-H distances of the C4 methyl group are long, 1.109A(2) compared to the case of **13** (1.090A(3)).. Oddly enough, in **14**, the distances are 1.107A(2) and 1.098A, which are not that different than for **11.**

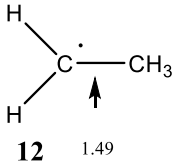
The calculated charge on CH_3 in **11** is +0.296 (using the Mulliken technique, with carbon and hydrogens summed) compared to zero for **13** and 0.001 for **14.** For **18**, CF_3 is calculated to have -0.373 charge compared to -0.10 for **17**, and +0.04 for **15**.

Scheme 6: Ethane Series with Fluorinated Derivatives



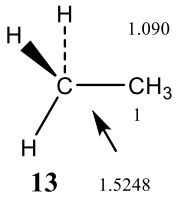
11 1.4147

50% C1 $sp^{1.69}$ 50% C4 $sp^{2.66}$
62% C1 $sp^{2.21}$ 38% H2 s



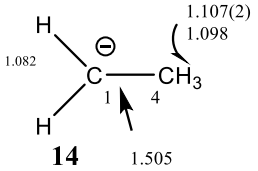
12 1.49

50% C1. sp $^{1.81}$ 50% C4 $sp^{2.65}$
62% C1 $sp^{2.13}$ 38% H2 s



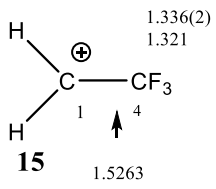
13 1.5248

50% C1 $sp^{2.58}$,
60% C1 $sp^{3.15}$ 40% H2 s



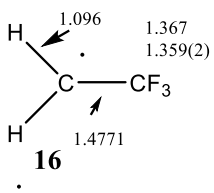
14 1.505

45% C1 $sp^{1.94}$ 54% C4 $sp^{1.96}$
59% C1 $sp^{2.05}$ 41% H2 s



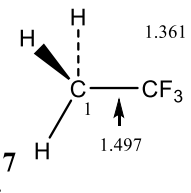
15 1.5263

52% C1 $sp^{2.16}$ 48% C4 $sp^{2.73}$
63% C1 $sp^{1.95}$ 37% H2 s



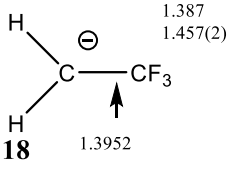
16 1.4771

45% C1 $sp^{2.25}$ 55% C4 $sp^{1.81}$
57% C1 $sp^{1.90}$ 43% H2 s



17 1.497

49% C1 $sp^{3.12}$ 51% C4 $sp^{1.77}$
62% C1 $sp^{2.95}$ 38% H2 s

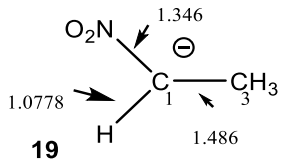


18 1.3952

48% C1 $sp^{2.05}$ 52% C4 $sp^{1.27}$
60% C1 $sp^{2.01}$ 40% H2 s

. The data of Scheme 7 show the effects of electronegative vs. electropositive groups (boron, in the latter case). Bonds from carbon to electronegative substituents (e.g. nitro in **20**) are quite short, with nitrogen being the principal "contributor". Bonds from carbon to electropositive substituents (e.g. boron in **21** and **22**) tend to be quite long with carbon being the principal "contributor". The C1-C4 bonds in the boron compounds also are somewhat extended. Comparison of **20** and **24** with **22** provides somewhat greater evidence for polarization. In both **20** and **24** the C1-C4 bond is composed of a greater "contribution" of C1, with C4 utilizing a "longer orbital" (high p character). In **22**, the "hybridizations" and "contributions" in the C1-C4 bond are similar.

Scheme 7: Comparison of Electronegative vs. Electropositive Groups

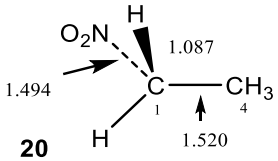


19

37% C1 $sp^{2.47}$ 63% N $sp^{1.46}$

49% C1 $sp^{1.76}$ 51% C3 $sp^{2.49}$

60% C1 $sp^{1.92}$ 40% H2 s

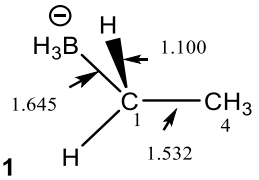


20

34% C1 $sp^{4.41}$ 66% N $sp^{1.74}$

52% C1 $sp^{2.39}$ 48% C4 $sp^{2.84}$

62% C1 $sp^{2.83}$ 38% H2 s

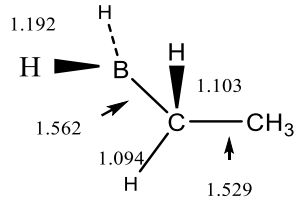


21

69% C1 $sp^{1.87}$ 31% B $sp^{3.01}$

48% C1 $sp^{3.04}$ 52% C4 $sp^{2.32}$

58% C1 $sp^{3.93}$ 42% H s

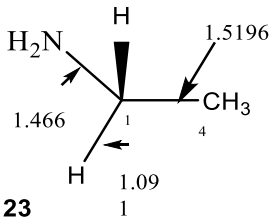


22

69% C1 $sp^{2.30}$ 31% B $sp^{1.97}$

51% C1 $sp^{2.63}$ 49% C4 $sp^{2.59}$

62% C1 $sp^{3.48 \text{ or } 4.02}$ 38% H s

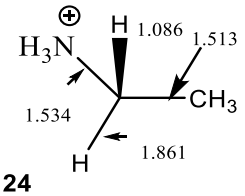


23

40% C1 $sp^{3.20}$ 60% N $sp^{2.20}$

50% C1 $sp^{2.56}$ 50% C4 $sp^{2.66}$

60% C1 $sp^{3.19}$ 40% H s



24

33% C1 $sp^{4.62}$ 67% N $sp^{2.44}$

52% C1 $sp^{2.29}$ 48% C4 $sp^{2.91}$

60% C1 $sp^{2.84}$ 40% H s

Finally, some data on calculated charge densities are given again (Scheme 8). The "sum" entry represents the sum of carbon plus attached hydrogens, whereas "C" represents the charge density on carbon by itself. Such calculated charge densities, of course, do not enjoy a good reputation.[63] The three methods of calculating charge density do not always agree in sign. Further, C7, seems out-of-line. If nitro were to remove electrons by the inductive effect, the attached carbon would be expected to show positive charge density. The "sum" entries provide a little greater credibility. The data do not uniformly suggest a diminishing positive charge density, as one moves down the chain.

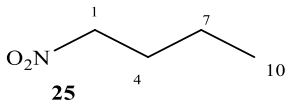
Using the MP2/6-31++G(d,p) calculation method, the gauche chain conformer **26** is calculated to be more stable than the zig-zag form **25**, by 0.7 kcal. Using MMX, **25** is found to be slightly more stable. To report data, one should not assume a single conformation to be the most important. A weighted average of important conformations should be used.

In Schemes 5-8, much depends on the validity of the NBO treatment of Glendenning, Reed, Carpenter and Weinhold. Let us hope that ability to interpret MO data soon improves so that resort to derived data is not necessary.

In conclusion, in CH_3X, where X is an electronegative group, there is undoubted electron withdrawal by X. For more extended chains, there is little evidence for methyl or methylene to serve as a sigma electron donor. The ability of hydrogen to donate or withdraw electrons is even less evident. Perhaps model (1) should be recast as 1' (excluding field effect).

$$CH_3\text{-}CH_2\text{-}CH_2\text{>}CH_2 \textbf{>X} \qquad \textbf{(1')}$$

Scheme 8: Calculated Charge Densities



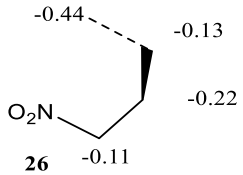
25

Mulliken

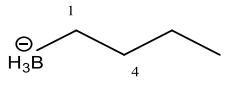
NO_2	N +0.18	C1 -0.231	C4 -0.283	C7 -0.145	C10 -0.466
	O -0.17	sum CH_x +0.122	+0.021	+0.088	-0.067
NPA					
NO_2	N +0.44	C1 -0.273	C4 -0.457	C7 -0.442	C10 -0.633
	O -0.35	sum CH_x +0.217	+0.015	+0.0	+0.03
	O -0.35				
CHELPG	N +0.68	C1 -0.120	C4 +0.038	C7 +0.171	C10 -0.231
	O -0.41	sum CH_x +0.02	+0.074	+0.13	-0.06
	O -0.41				

Mulliken

N +0.238
O -0.237
O -0.259



26



27

C1	-0.60	C4	-0.053	C7	-0.19	C10	-0.44
sum CH_x	-0.38		+0.17		-0.03		-0.10

Energy difference (**26 - 25**)

-0.70 kcal (mp2/6-31++G(d,p))
+0.2 kcal (MMX)

Methods:

The computational program used was Gaussian03.[91] Frequencies were not always determined. The NBO calculations occasionally did not complete as the program determined that a negative value of

one parameter was present. The data presented stem from an earlier part of the calculation sequence (about 3 cases). These data are included but no important conclusion was drawn. MMX or MM3 data were taken from PCModel calculations.[92]

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